

## Supporting Information

### **Vinylene-linked fully conjugated porous organic polymers based on difluoroboron $\beta$ -diketonate complexes for green and efficient photocatalysis**

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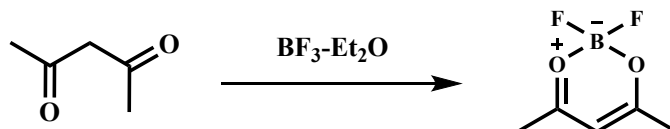
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## Section 1. Syntheses

### Synthesis of (T-4)-Difluoro(2,4-pentanedionato- $\kappa$ O2, $\kappa$ O4)boron(B1)<sup>1</sup> :



Dissolve acetylacetone in anhydrous dichloromethane. Add dropwise 1.5 equivalents of boron trifluoride diethyl etherate to the mixture. Heat the reaction mixture under reflux for 5 hours under a constant nitrogen gas flow until full conversion is reached. Cool the mixture to room temperature. Add 50 mL of water to the mixture to quench the reaction, then stir for an additional ten minutes. Separate the organic phase and wash with water. Dry the mixture over magnesium sulfate. Evaporate the solvent to obtain the product. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  6.39 (s, 1H), 2.34 (s, 3H).

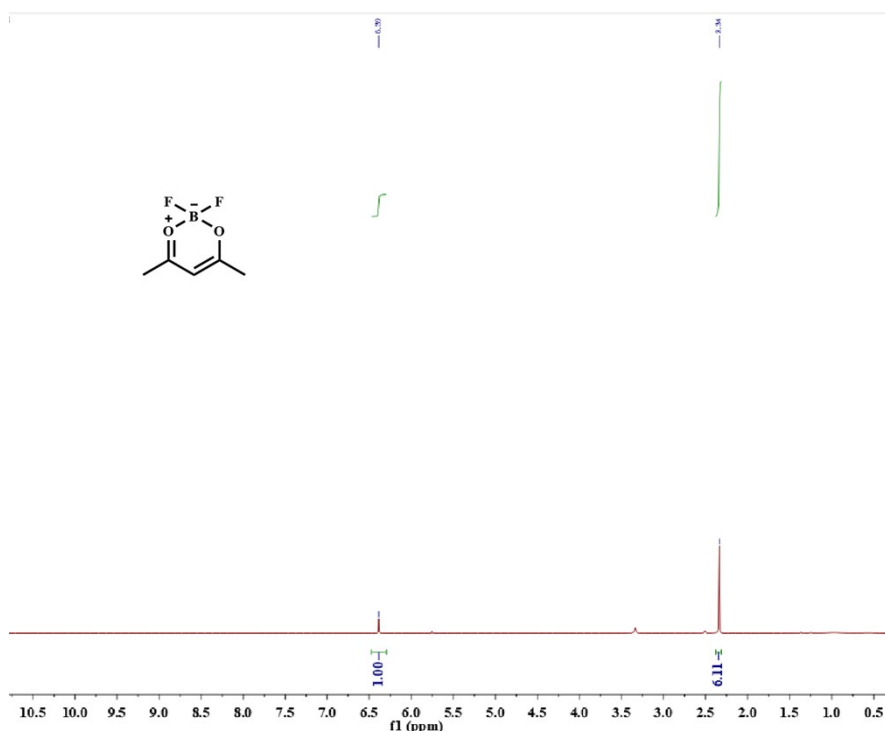
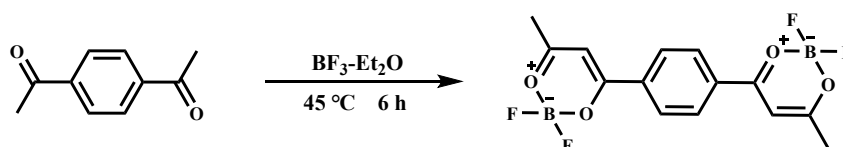


Fig. S1 <sup>1</sup>H NMR spectra (DMSO, 400 MHz, rt) of B1.

### Synthesis of Boron, tetrafluoro [ $\mu$ -[[1,1'-(1,4-phenylene) bis [1,3 - butanedionato- $\kappa$ O: $\kappa$ O'] ] (2-)](B2)<sup>2</sup>:



To a stirred solution of 0.81 g (5 mmol) of 1,4-diacetylbenzene in 1.4 mL of acetic anhydride, 2.8 mL (20 mmol) of BF<sub>3</sub>-AcOH complex was added dropwise under nitrogen at 45 °C. The mixture was stirred at this temperature for 6 hours. The product was worked up according to the published procedure, yielding 1.22 g of yellow crystals. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 8.36 (s, 4H), 7.44 (s, 2H), 2.54 (s, 6H).

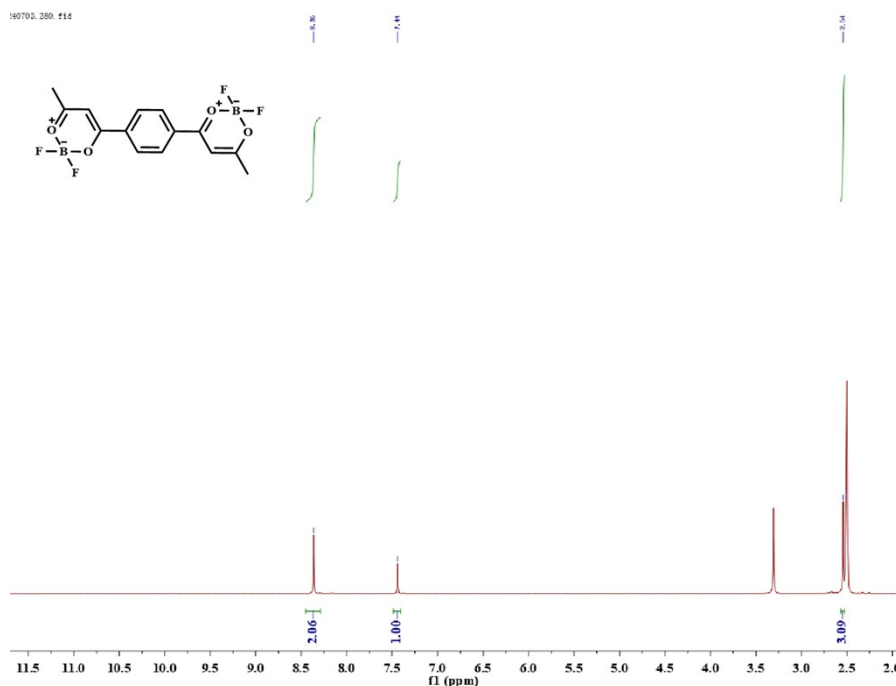
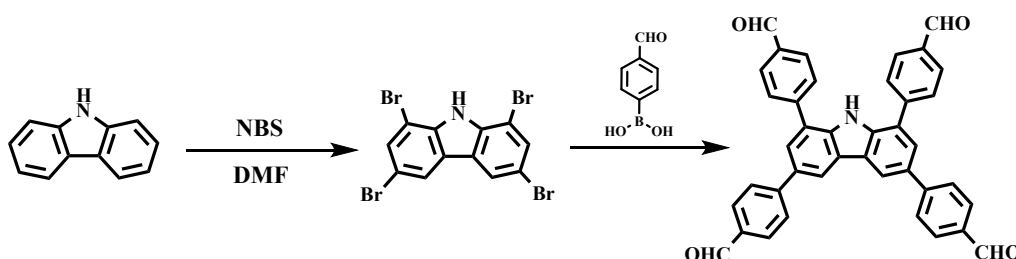


Fig. S2 <sup>1</sup>H NMR spectra (DMSO, 400 MHz, rt) of B2.

### Synthesis of 4,4',4'',4'''-(9H-carbazole-1,3,6,8-tetrayl) tetrabenzaldehyde (CTBA)<sup>3</sup>:



Carbazole and DMF were mixed in a flask and stirred in an ice bath under nitrogen for 1 hour to prepare solution A. N-Bromosuccinimide (NBS) and DMF were mixed and stirred to form solution B. Solution B was slowly added to solution A and the reaction was allowed to proceed for 12 hours. At the end of the reaction, deionized water was added to the mixture. The resulting precipitate was filtered, washed, and dried. The crude product was then recrystallized from ethanol to obtain 1,3,6,8-tetrabromo-9H-carbazole.

1,3,6,8-tetrabromo-9H-carbazole, 4-formylphenyl boronic acid, potassium carbonate, and palladium tetrakis(triphenyl phosphine) were added to a 250 mL Schlenk tube equipped with a stir bar and condenser. Dioxane and deionized H<sub>2</sub>O were mixed and then added to the Schlenk tube. The mixture is then bubbled under nitrogen for 30 minutes. The reaction mixture was then heated to reflux for 3 days. After cooling to room temperature, concentration under reduced pressure yields a black-green solid. The product was then washed with large amounts of dichloromethane and water and recrystallized from ethanol. Yield: 60%. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>): δ 11.54 (s, 1H), 10.18-10.08 (m, 4H), 8.90-8.88 (d, *J* = 8.0 Hz, 2H), 8.50 (s, 2H), 8.14-8.12 (d, *J* = 8.0 Hz, 4H), 8.07-8.05 (d, *J* = 8.0 Hz, 4H), 7.99-7.97 (d, *J* = 8.0 Hz, 4H), 7.94-7.92 (d, *J* = 8.0 Hz, 4H), 7.70-7.68 (d, *J* = 8.0 Hz, 2H).

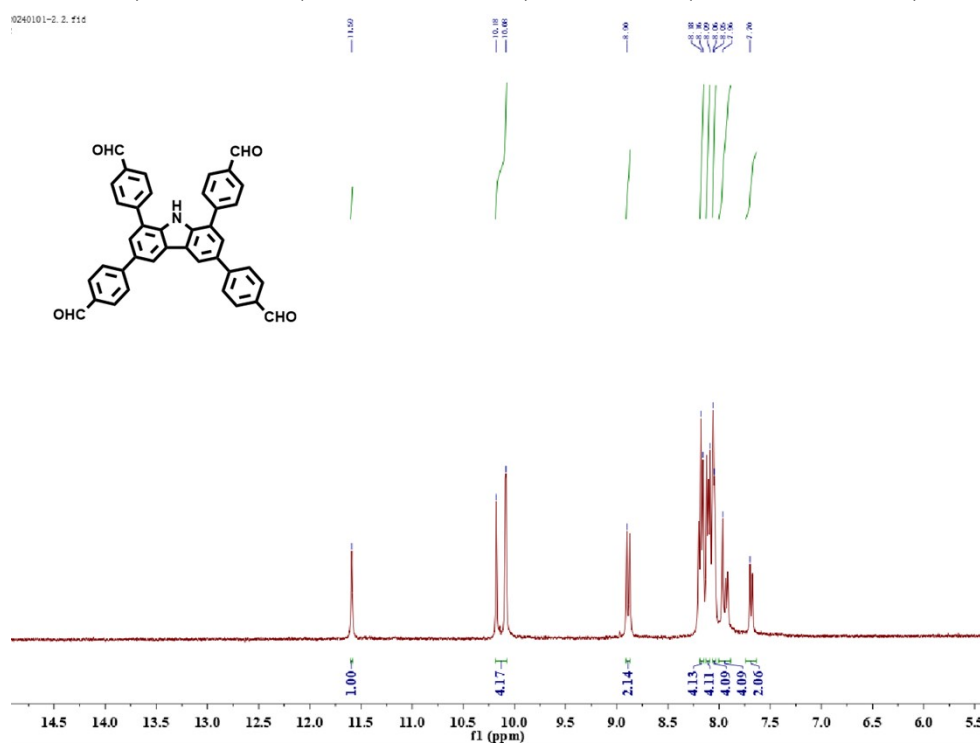


Fig. S3 <sup>1</sup>H NMR spectra (DMSO, 400 MHz, rt) of CTBA.

### Synthesis of porous organic polymers(CTBA-B1 and CTBA-B2):

As shown in Scheme 1, 0.075 mmol of boron-containing monomer and 0.05 mmol of 4,4',4'',4'''- (9H-carbazole-1,3,6,8-tetrayl) tetrabenzaldehyde were added to the Schlenk tube, followed by 2 ml of DMF and 0.3 mmol of piperidine. The mixed solution was sonicated for half an hour to mix it well. After sonication the solution was subjected to three freeze-pump-thaw cycles. The reaction was then placed in an oil bath at 180 °C for three days. After the reaction, filter the precipitate and wash it with DMF, dichloromethane, and ethyl acetate. Then, perform a Soxhlet extraction

using methanol and tetrahydrofuran for three days. Finally, it was dried to obtain the brownish-yellow product.

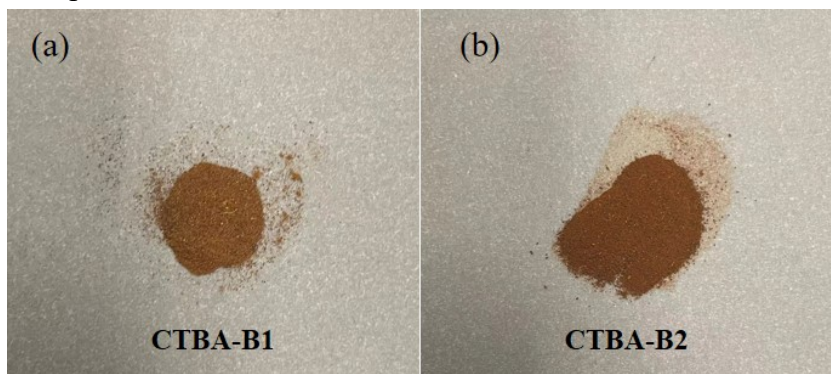


Fig. S4 Photographs of CTBA-B1 and CTBA-B2.

## Section 2. $^{13}\text{C}$ CP/MAS NMR

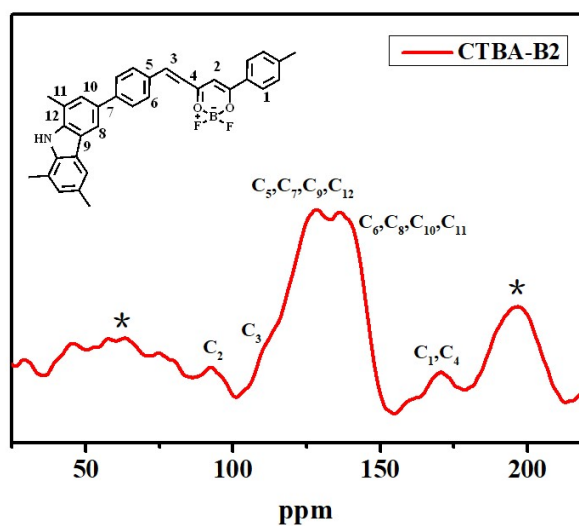


Fig. S5  $^{13}\text{C}$  CP/MAS NMR spectra of CTBA-B2.

## Section 3. Pore size distribution

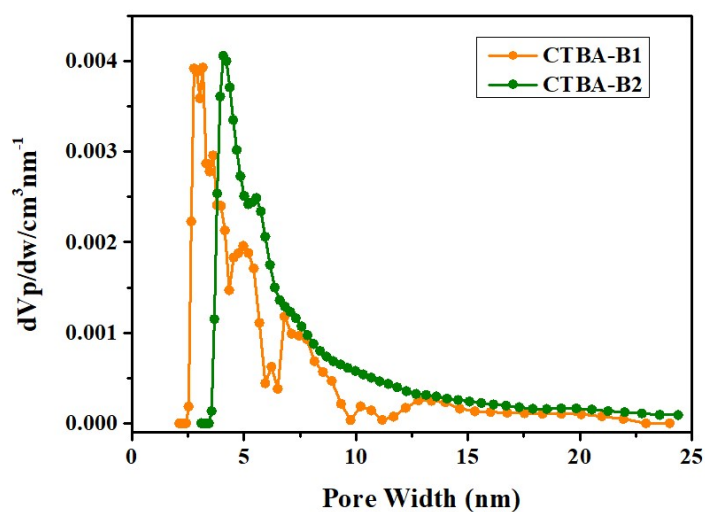


Fig. S6 Pore size distribution of CTBA-B1 and CTBA-B2.

## Section 4. SEM Image

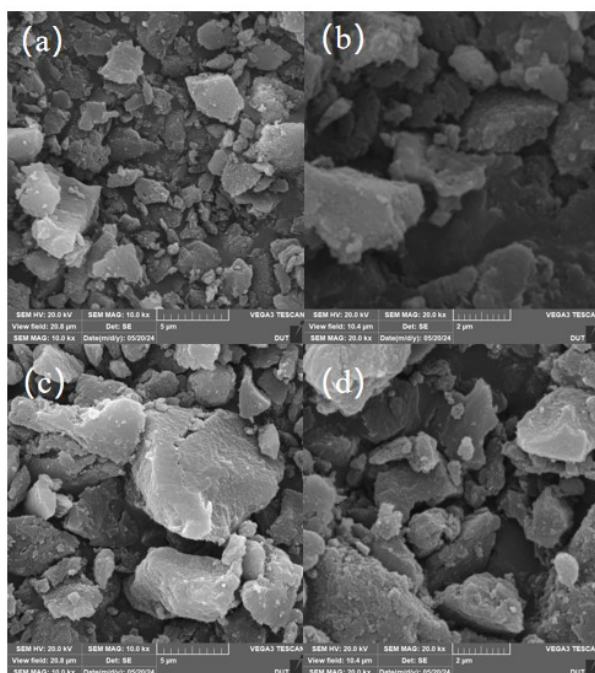


Fig S7 SEM images of (a), (b) CTBA-B1 and (c), (d) CTBA-B2.

## Section 5. Mott-Schottky curve

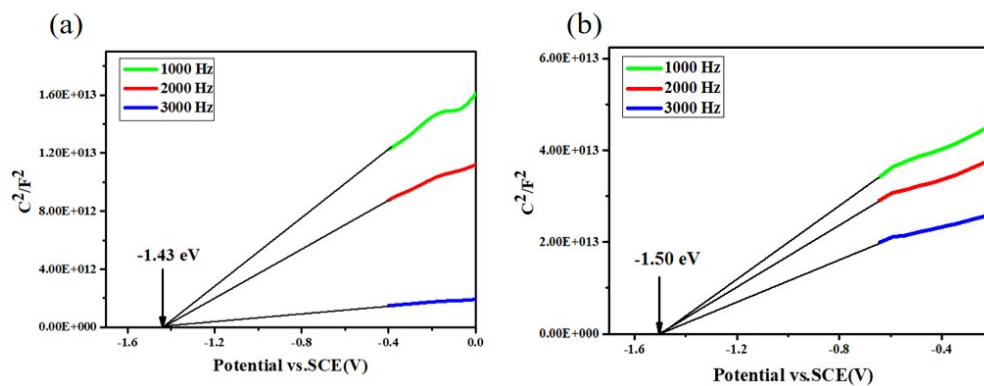


Fig. S8 Mott-Schottky plots of (a) CTBA-B1 and (b) CTBA-B2.

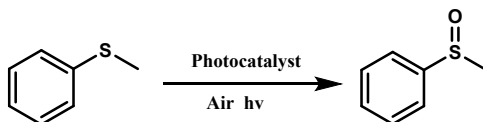
## Section 6. Photocatalytic machine



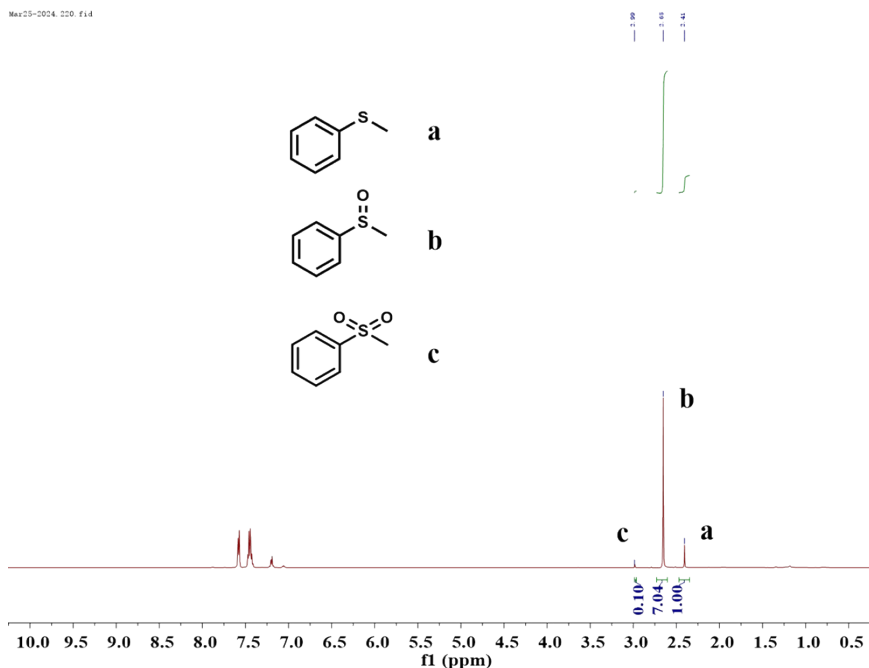
Fig. S9 WP-TEC-1020HSL photochemical reaction system.

## Section 7. Characterization Data of Catalytic Products

### Oxidation of sulfides:

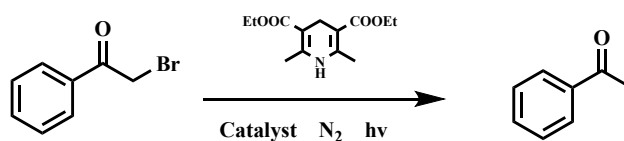


A mixture of CTBA-B2 and sulfide (0.5 mmol) in EtOH (2 mL) was stirred under air at room temperature over 10 W blue LED irradiation. After completion of the reaction the catalyst was filtered, washed and dried. The product was concentrated under reduced pressure to remove the solvent. The crude product was analyzed by  $^1\text{H}$  NMR and the ratio between the integral peaks of the starting material and the product was used to calculate the conversion.<sup>4-6</sup>



**Fig. S10**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 400 MHz, rt) of sulfide oxidation mixture.

### Dehalogenation reaction:



A mixture of CTBA-B2 and  $\alpha$ -bromoacetophenone (0.2 mmol), hansyl ester (0.22 mmol), and DIPEA (0.4 mmol) in EtOH (2 mL) was stirred at room temperature in  $\text{N}_2$  while irradiated with a 10 W green LED. After completion of the reaction the catalyst was filtered, washed and dried. The product was concentrated under reduced pressure to remove the solvent. The crude product was analyzed by  $^1\text{H}$  NMR and the yield was calculated using dibromomethane as an internal standard.<sup>7-10</sup>

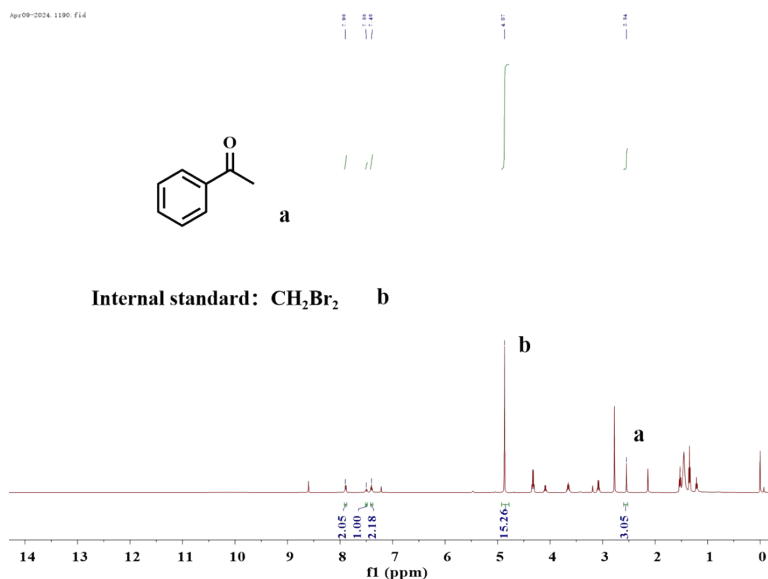




Fig. S11  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 400 MHz, rt) of dehalogenation reaction mixture.

## Section 8. Recyclability and stability

### The operational procedures for the catalytic cycling experiment:

After completing a catalytic experiment, the catalyst was filtered out and washed with dichloromethane and ethanol. The washed polymer was then vacuum-dried and prepared for the next catalytic experiment.

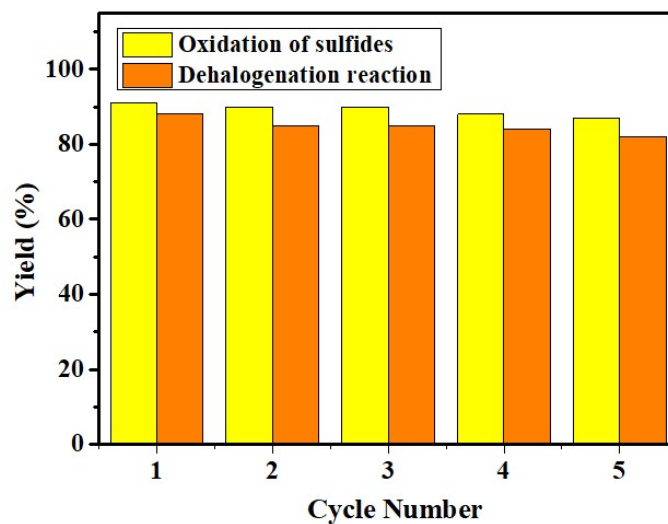


Fig. S12 Recyclability of CTBA-B2 in oxidation of sulfides and dehalogenation reaction. The reaction time was fixed for each cycle.

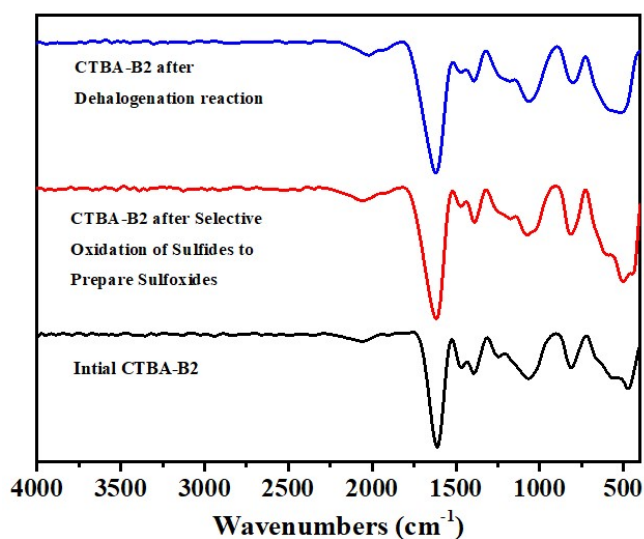


Fig. S13 FT-IR spectra of before and after CTBA-B2 catalysis.

## Section 9. Reference :

### References:

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